PRODUCTION OF BIO FUEL FROM PYROLYSIS OF JATROPHA SEED

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Certificate

This is to certify that the thesis entitled **"production of bio fuel from pyrolysis of Jatropha seed"** submitted by **Mr. Siba Sankar Sethi (109CH0094)** in partial fulfillment of the requirements of the prescribed curriculum for Bachelor of Technology in Chemical Engineering Session 2009-2013 to the National Institute of Technology, Rourkela is an authentic project work, carried out by him in the Department of Chemical Engineering under my supervision and guidance. To the best of my Knowledge the work carried out by him is authentic. The results embodied in the thesis are full of facts and have not been submitted for the award of any other degree.

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ABSTRACT

Bio-energy is now accepted as having the potential to provide the major part of the projected renewable energy provisions of the future. Though there are many conversion processes like pyrolysis, gasification, combustion and liquefaction, pyrolysis has gained special attention as it can convert it directly into liquid, solid and gaseous products by thermal decomposition in absence of oxygen. Pyrolysis is one of the three main thermal paths, along with gasification and combustion, for providing useful and valuable bio-fuel. Jatropha seed are high energy bearing seeds available in nature. Thermal pyrolysis of this was carried out in a semi batch reactor made up of stainless steel at temperature ranging from 350^{o}C to 600^{o}C to produce bio-fuelat an interval of 50^{o}C. The effect of temperature on pyrolysis of the material is studied to know the optimum temperature for maximum liquid yield. The thermal degradation of the Jatropha seed was studied using thermo gravimetric analysis (TGA) at a heating rate of 20^{o}C/min in air atmosphere which indicated the range of temperature in which rate of decomposition is maximum. The oil and char obtained at optimum temperature was analyzed according to their elemental analysis, fuel properties, functional groups present, and compounds' presence. The result so obtained is compared with the commercial fuel. Fuel properties like specific gravity, cloud point, kinematic viscosity, flash point, fire point, pour point and were also determined. The chemical compositions of the bio-oils and char were investigated using FTIR, and GC-MS. Surface morphology was studied using SEM analysis.

***Keywords:* -** Jatropha seed, De-oiled cake, bio-oil, Bio diesel, pyrolysis, TGA, Proximate analysis, Ultimate analysis, FTIR, SEM, GC-MS.

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CHAPTER 1

INTRODUCTION

With the explosive growth of population energy demand is growing exponentially now a days. Since fossil fuel resources are declining and demand for their products are increasing, there is an urgent need to develop economical, energy-efficient processes and resources for the production of fuels and chemicals. Renewable biomass is now being considered as an important energy resource all over the world. Indeed there are a number of biomass sources being considered as potential sources of fuels and chemical feedstock.

Biomass is the abundant unexplored source of energy mostly comprising of cellulosic and non cellulosic matter found in the biodegradable material from energy crops, agriculture, forest wastes, industrial effluents, animal wastes etc. Biomass, which contributes to one-seventh of the world-wide energy consumption and for as much as 43% of the energy consumption in some developing countries, has a great potential to be a renewable source of energy. The increase in the emissions rates of greenhouse gases produced from the use of these fossil fuels presents a threat to the world climate. All biomass products can be converted into commercial fuels which can be goo substitute for fossil fuels. These can be used for heating, electricity generation, transportation, or anything else where fossil fuels are used. The conversion is accomplished by using several distinct and simple processes. These processes include both thermal conversions and biochemical to produce gaseous, liquid and solid fuels that have high energy contents. These are easily transportable and therefore suitable to be used as commercial fuels. Thermo chemical processes are thought to have great promise as a means for efficiently and economically converting biomass to synthetic fuels. Among the thermochemical processes, pyrolysis has been quite popular since the process can be performed under a variety of conditions to capture all the components and to maximize the output of the desired product, be it chars liquid or gas. Pyrolysis is a thermal decomposition process that takes place in the absence of oxygen to convert biomass into liquid products, solid charcoal, and gases at higher temperatures. The liquid fuel obtained by the pyrolysis of these raw material can also be upgraded into quality fuels, added to petroleum refinery feedstock or various value added chemicals can be recovered economically.

Biomass has very high potentials of being a promising green energy source with negligible sulfur and nitrogen content. The reason for its popularity is its abundant supply and ease in farming culture. It has the potential to supply 10–14% of world's total energy if utilized properly. In ancient period, biomass was used in rural areas for cooking and heating purposes but the process was very inefficient and polluting as the biomass had high moisture content and very less density. Biomass can be utilized efficiently and hence increase its credibility by employing pre- treatment techniques and implementation of proper technologies such as gasification, pyrolysis, carbonization and fermentation. Among these, pyrolysis is of great importance as all the products obtained by this process, namely char (solid remaining), oily water, biofuel (liquid products) and fuel gas (non-condensable vapors), have higher market value.

Here the form biomass to be used is the Jatropha seed. This grows wildly in many areas of India and even found on infertile soil. A good crop can be obtained with a little effort. Depending on soil quality and rainfall, oil can be extracted from the jatropha nuts after two to five years. These cakes are used and biofuel is extracted from them using semi batch reactor.

CHAPTER 2
LITERATURE REVIEW

2.1 BIOMASS

Biomass refers to any organic materials that are derived from plants or animals. In general it is difficult to find out the generalized definition. Biomass is biodegradable and non-fossilized organic material basically originating from animals, plants and micro-organisms. This involves the residues, products, byproducts, and wastes from forestry, agriculture, municipal ans industrial wastes. Biomass can also include gases and liquids recovered from the decomposition of non-fossilized and biodegradable organic materials. Since plants use carbon dioxide at the time of photosynthesis process for making their own food, the amount of CO_2 does not increase in the earth. Thus, it is called greenhouse gas neutral. It does not include organic materials that converted to coal or petroleum over many millions of years by geological processes. Biomass comes from botanical (plant species) or biological (animal waste or carcass) sources, or from a combination of these [3].

2.2 CONSTITUENTS OF BIOMASS

The major constituents of biomass are lignin, cellulose and hemicelluloses [2].

2.2.1 CELLULOSE

The primary organic component of the cell wall of the biomass is cellulose. It is represented by generic formula $(C_6H_{10}O_5)_n$. Cellulose is having crystalline and strong structure that can resistant hydrolysis and is a long chain polymer with a high degree of polymerization (~10,000) and a large molecular weight (~500,000). Cellulose is primarily composed of d-glucose, which is made of six carbons. This is highly insoluble, though it is a carbohydrate that not digestible by humans. It is a prime component of wood making up about 40 to 44% by dry weight. Its amount varies from 90% (by weight) in cotton to 33% for most other plants [3].

2.2.2 HEMICELLULOSE

The constituent of the cell wall of the plant is hemicelluloses and represented by the generic formula $(C_5H_8O_4)$ n. It is a group of carbohydrates with a branched chain structure and a lower degree of polymerization [3].

2.2.3 LIGNIN

The third important constituent of woody biomass is lignin, which is complex in nature, highly branch polymer of phenyl propane and is an integral part of the secondary cell walls of plants. It is primarily a three dimensional polymer of 4-propenyl phenol, 4-propenyl-2-methoxy phenol, and 4-propenyl-2,5-dimethoxyl phenol. It is one of the most abundant organic polymers on Earth (exceeded only by cellulose). Lignin is the cementing agent for cellulose fibers holding adjacent cells together. The dominant monomeric units in the polymers are benzene rings [3].

2.3 BIO FUEL

Bio-fuels are produced from living organisms or from metabolic by-products (organic or food waste products). In order to be considered a bio-fuel the fuel must contain over 80 percent renewable materials. It is originally derived from the photosynthesis process and can therefore often be referred as a source of solar energy. The term bio fuel covers solid biomass, liquid fuels and gaseous fuel. Solid bio-fuel includes wood, sawdust, grass cuttings, domestic refuse, charcoal, agricultural waste, non-food energy crops and dried manure where biodiesel, bioalcohol, bio-ether, pyrolytic oil are liquid bio-fuel and syngas and bio gas are gaseous bio-fuel [4].

2.4 METHODS OF THERMAL CONVERSION OF BIOMASS TO BIO-FUEL

Biomass can be converted into solid, liquid and gaseous fuels by a number of processes. The technologies include thermal, thermo-chemical and bio-chemical conversions. The actual processes in these technologies are alcoholic fermentation, combustion, pyrolysis, gasification, liquefaction etc [4].

2.4.1 PYROLYSIS

Pyrolysis is one of the best methods to convert all biomass materials into bio oil, char and volatiles. Pyrolysis is the process of heating of organic materials the absence of air or oxygen at high temperature of 500 – 1100^{o}C. The bio oil obtained by this process contains 10-20% water [11]. Bio-oil is produced by rapidly and simultaneously depolymerizing and fragmenting the cellulose, hemicelluloses, and lignin components of biomass. In a typical operation, the biomass is subjected to a rapid increase in temperature followed by an immediate quenching to freeze the intermediate products obtained in pyrolysis. Rapid quenching is important since it prevents

further cleavage, degradation, or reaction with others. Bio oil is a micro emulsion, in which the continuous phase is an aqueous solution of the products such as cellulose and hemicelluloses decomposition and small molecules from decomposition of lignin. The discontinuous phase is largely composed of pyrolytic lignin macromolecules [12]. These bio oils can be used as fuel for transportation purposes. The compounds presents in bio-oil fall into the following five broad categories [11]. They are:

- Hydroxyaldehyde
- Hydroxyketones
- Sugars and dehydrosugars
- Carboxylic acids
- Phenolic compounds

Bio-oil is produced by rapidly and simultaneously depolymerizing and fragmenting the cellulose, hemicelluloses, and lignin components of biomass. The nature of the product depends on several factors such as pyrolysis temperature and rate of heating and catalyst etc. The condensable may break down further into non condensable gases namely CO, CO_2, H_2, and CH_4, liquid, and char.

2.5 TYPES OF PYROLYSIS

This process pyrolysis occurs in three different ways, namely fast pyrolysis, slow pyrolysis and flash pyrolysis.

2.5.1 FAST PYROLYSIS

In fast pyrolysis process the feed stock is rapidly heated at a high rate of heating in absence of oxygen/air at high temperature. During this decomposition process, biomass generates aerosols, vapors, and some charcoal like char. After cooling and condensation of the vapors and aerosols, a dark brown mobile liquid is formed that has a heating value that is about half that of conventional fuel oil. Fast pyrolysis is a more advanced process that can be carefully controlled to give high yields

of desired liquid products [15]. Fast pyrolysis process produces 60-75 wt % of liquid bio oil, 15-25 wt % of solid char, and 10-20 wt % of non-condensable gases, depending on the feed stock used [5].

2.5.2 SLOW PYROLYSIS

Sometimes slow pyrolysis is also referred as conventional pyrolysis. When pyrolysis is carried out at slow heating rate (3-7K/min), it is regarded as slow pyrolysis [5].

2.5.3 FLASH PYROLYSIS

In case of flash pyrolysis biomass is heated rapidly in the absence of oxygen to a relatively modest temperature range of 450 to 600 °C where the reaction time is 30 to 1500 ms [5]. Upon cooling, the condensable vapor is then condensed into a liquid fuel known as bio-oil. Such an operation increases the liquid yield while reducing the char production. A typical yield of bio oil in flash pyrolysis is 70 to 75% of the total pyrolysis product.

2.6 PRODUCTION OF BIOFUEL FROM DEOILED MAHUA CAKE

Pyrolysis of mahua cake was carried out at in a semi batch reactor at different temperatures (350,400,450,500,550,600^{o} C) and the optimum temperature in which bio crude formation is maximum was found out. The optimum temperature at which maximum yield of 41.36% (by weight) liquid product obtained was 550deg.C. Empirical formula of the bio-oil was determined and accepted as $CH_{1.379}N_{0.0576}S_{0.004}O_{0.614}$. The thermal degradation of mahua de-oiled cake was studied in inert atmosphere from ambient temperature to a temperature of 600 ^{o}C at a heating rate of 25^{o}C/min. The char obtained at a pyrolysis temperature of 550^{o}C was characterized for its surface area and was found to be nearly 10.2 m^2/g. Lower surface area explains the lower reactivity of the char. The liquid obtained was characterized using FTIR analysis to find out presence of various functional groups. Various tests were conducted to find out various physical properties like density, calorific value, viscosity, flash point, pour point etc. The chemical composition of bio-char was investigated by using SEM-EDX and its heating value was determined to be 26 MJ/kg. SEM analysis was done to find the morphology of the mahua char. The image was taken different magnifications showed rough texture on its surface with heterogeneous distribution of pores. The average pore diameter was found out which shows that it can be used as adsorbent. White colored spots on char shows the presence of residual ash. Analysis using EDX of the mahua char shows the presence of Mg, K, Cl, and P. BET surface area analysis of char was carried out because, like other physio-chemical characteristics, devolatilization temperature, heating rate may strongly affect the reactivity and combustion behavior of the char.

2.7 BIOCRUDE FROM BIOMASS: PYROLYSIS OF COTTON SEED CAKE

This literature reveals that fixed bed pyrolysis of cotton seed cake can be carried out in various reactors, namely a tubular. Pyrolysis atmosphere and pyrolysis temperature effects on the pyrolysis product yields and chemical composition have been investigated. The maximum oil yield of 29.68% was obtained in N_2 atmosphere at a pyrolysis temperature of 550°C with a heating rate of 7°C/ min. in a tubular.

At first, to determine the effect of the pyrolysis temperature and the heating rate on the cottonseed cake pyrolysis yields, 40 g of air-dried cake was cracked in the reactor. The flow of the gas released was measured using a soap film for the duration of the experiments. The liquid phase was collected in a glass liner located in a cold trap maintained at about 0°C. The liquid phase consisting of aqueous and oil phases which were separated and weighed. When pyrolysis was over, the solid char was removed and weighed, and then the gas yield was calculated by the difference.

The second group of experiments was also performed in the Heinze reactor in order to establish the effect of sweep gas velocity on the pyrolysis yields, under a nitrogen atmosphere. The experiments were conducted at sweep gas flow rates of 50, 100, 200, or 400 cm^3/ min. For all these experiments, the heating rate and the final pyrolysis temperature were 7°C/ min and 550°C, respectively, based on the results of the first group of experiments [12].

The third group of experiments was performed in the well-swept tubular reactor to determine the effect of the pyrolysis temperature and sweeping gas flow rates on the pyrolysis yields. 10 g of sample was placed in the reactor and sweep gas was controlled and measured by a rotameter. The experiments were carried out with a temperature increment of 7°C min^{-1} to the final temperature of 400, 450, 500, 550, or 700°C under nitrogen atmosphere. The sweep gas flow rates were 50, 100, 200, 400 cm^3/min.

Proximate and elemental analyses were carried out on the cotton seed cake. The oils analysed in this study have been obtained under experimental conditions that gives maximum oil yield. The elemental compositions and calorific values of the pyrolysis oils were determined. The 1H NMR of the same oils was obtained at a H frequency of 90 MHz using a Jeol EX 90A instrument. The sample was dissolved in chloroform-d. The IR spectra of the oils were recorded using a Jasco FTIR Infrared Spectrophotometer. Chemical class composition of the oils was

determined by liquid column chromatographic fractionation. Char and bio fuel were characterized.

2.8:- PROPERTIES AND FUEL USE OF BIOMASS DERIVED FAST PYROLYSIS LIQUIDS:

Biomass fast pyrolysis liquids are completely different from petroleum fuels in their physical properties and chemical composition. These liquids are typically rich in water, can have substantial levels of suspended solids which have density higher than conventional fossil fuels, are acidic, have a heating value of about half of that of mineral oils, and are chemically unstable when heated. Pyrolysis liquids are highly polar, containing about 35–40 wt% oxygen (dry basis), while mineral oils contain oxygen at ppm levels. Pyrolysis liquids are not miscible with mineral oils. The unusual properties of the liquids must therefore be taken into careful consideration in a range of applications.

Table.2.8:- properties of bio oil [28]

Water, wt%	20-30
Solid, wt%	<0.5
Ash, wt%	0.01-0.2
Nitrogen, wt%	<0.4
Sulphur, wt%	<0.05
Flash point, deg.C	40-110
Pour point, deg.C	9-36

The chemical composition of fast pyrolysis liquids is difficult to analyze with conventional methods like GC/MSD due to low volatility resulting from the polarity and high molecular mass of the compounds in the liquid. A solvent fractionation scheme based on water-extraction was developed for chemical characterization of whole pyrolysis liquids. In the method, pyrolysis liquid is divided into water-soluble (WS) and water insoluble (WIS) fractions. The WIS fraction can further be separated by dichloromethane (DCM) extraction into two fractions with having different molecular size distributions. The water insoluble materials consist mainly of lignin material, extractives (neutral substances) and solids. In aged liquids, this fraction also includes high-molecular-mass reaction products mainly derived from the pyrolytic

lignin. The water soluble (WS) fraction consists mainly of water, sugars (sugar type compounds, ether insoluble), acids, ketones, aldehydes, furans and pyrans.

2.9:- BIOREFINERIES FOR BIOFUEL UPGRADING: A CRITICAL REVIEW

This study reviews the biofuel valorization facilities as well as the future importance of bio refineries. Biofuel obtained from biomass can be upgraded to various chemicals and quality fuels which can be used in combustion engines as well as power plants. Biomass upgrading processes include hydrolysis, fermentation, fractionation, liquefaction, pyrolysis, and gasification. The benefits of an integrated bio refinery are numerous because of the diversification in products and feed stocks as well. There are presently several different levels of integration into bio refineries which improve their sustainability and reliablity, both economically and environmentally. The economic and production advantages increase with the level of integration in the bio refineries.

2.9.1:-FRACTIONATION VALORIZATION TECHNOLOGIES OF WOOD AND WOODY BIOMASS

Fractionation refers to the conversion of wood into its constituent components (cellulose, hemicelluloses, and lignin). Processes include aqueous separation; hot water systems and steam explosion. Commercial products of biomass fractionation include levulinic acid, xylitol, and alcohols. Biofuels can be classified based on their production technologies: first generation biofuels (FGBs); second generation biofuels (SGBs); third generation biofuels (TGBs); and fourth generation biofuels [11].

First generation biofuels (FGBs) refer to biofuels which are made from vegetable oils, starch, sugar, or animal fats using conventional technology. FGBs produced from food crops such as sugar beet, and oil seeds, grains are limited in their ability to achieve targets for oil product climate change mitigation, substitution, and economic growth. Second generation biofuels are made from non-food crops, wheat straw, corn, wood, energy crop by the use of advanced technology. Algae fuel, also called oilgae or third generation biofuel, is a biofuel from algae. On the contrary, an appearing fourth generation is based in the conversion of veg oil and bio-diesel into bio gasoline using various advanced technologies [11].

The bio refinery concept attempts to apply to biomass conversion same as the methods that have been applied to the refine the petroleum fractions. Bio refineries would simultaneously

produce biofuels as well as bio-based chemicals, heat, and power. Bio refineries would present more economical option where bio-based chemicals are co-products of liquid fuel. Future bio refineries would be able to mimic the energy efficiency of modern oil refining through extensive heat integration and coproduct development. Heat that is released from some processes within the bio refinery could be used to meet the heat requirements for other processes in the system. There is a number of pilot-scale and demonstration plants either operating, under development [11].

2.9.2:-FISCHER–TROPSCH SYNTHESIS OF SYNGAS FROM BIORENEWABLES:

Fischer–Tropsch Synthesis from syngas is obtained by gasifying the biomass. The main aim of this is synthesis of long-chain hydrocarbons from CO and H_2 gas mixture at suitable conditions.

$$nCO + \left(n + \frac{m}{2}\right) H2 \rightarrow CnHm + nH2O$$

Where n is the average length of the hydrocarbon chain and m is the number of hydrogen atoms need per carbon. All reactions are exothermic and the product is a mixture of different hydrocarbons in that paraffin and olefins are the main parts. Syngas includes mainly hydrogen and carbon monoxide which is also called as syngas (H_2 + CO). Methanol can be produced from hydrogen-carbon oxide mixtures by means of the catalytic reaction of carbon monoxide and some carbon dioxide with hydrogen. Copper– zinc and chrome–zinc catalysts are used in industrial methanol production. Bio-syngas is a gas rich in CO and H_2 obtained by gasification of biomass. The aim of FT is synthesis of long-chain hydrocarbons from CO and H_2 gas mixture. Liquid biofuels such as bioethanol and biodiesel are important for the future because they replace petroleum fuels. The liquid biofuel derived from renewable sources of feedstock; typically plants such as sugar beet, corn, wheat, straw, and wood; is called as bioethanol [11].

CHAPTER 3

EXPERIMENTAL SECTION

3.1 RAW MATERIAL:

The Jatropha seed samples are collected. These seeds are crushed into small sizes and kept in the oven for 5-6 hrs at of temperature of 60-70℃. These are used as feed.

Fig.3.1:-Jatropha seed

3.2 THERMAL PROPERTIES OF RAW MATERIALS USING TGA

The thermo gravimetric analysis (TGA) of raw material was done using the DTG 60 instrument. The apparatus uses a horizontal differential system balance mechanism. 6-8 mg of sample was taken for analysis. Sample was placed in a platinum container. TGA was carried out at heating rate of 20℃/min. in presence of atmospheric air. The sample was heated up to final temperature of 700℃. The thermo gravimetric weight loss curve (TG, Wt %) was recorded as a function of temperature. The TGA analysis of the sample (jatropha seed) was analyzed. The TGA analysis of different sample depends on the amount of cellulose, hemicelluloses and lignin content of the sample.

3.3 CHARACTERIZATION OF RAW MATERIALS

3.3.1 PROXIMATE ANALYSIS:

Proximate analysis (defined by ASTM), is the determination of moisture, volatile matter, fixed carbon (by difference) and ash by prescribed methods. This is primarily carried out to ascertain the quality of the feed. It gives quick and valuable information regarding commercial classification and determination of suitability for particular industrial use.

- **Moisture:** It increases transportation cost, reduces calorific value. A 10 gm of sample taken on a Petridis and kept at 108℃ for 90 minutes and loss in weight is expressed in percentage.
- **Volatile matter:** It is a complex mixture of various organic and inorganic gaseous and liquid products result from thermal decomposition. The smoke forming tendency, length of flame and ignition characteristics are related to this. 1.5 gm of sample kept at 925±15 ℃ with a crucible having lid for 7 minutes duration and loss weight gives the volatile matter percentage.
- **Ash content:** It is the final residue left after the complete combustion of sample. It is found out by heating 1 gm of sample at 750±15 ℃ for one and half hour without lid. The weight of residue in the crucible is expressed as the ash content.
- **Fixed carbon:** Moisture, volatile matter, ash content together subtracted from 100 gives the fixed carbon content.

3.3.2 ULTIMATE ANALYSIS:

The ultimate analysis of the material was carried out in CHNSO elemental analyzer (Vario El Cube Germany) to know the elemental composition.

3.4 EXPERIMENTAL SET UP:

Fig. 3.4 shows the schematic diagram of the set up used for biomass pyrolysis experiment. The pyrolysis unit consists of pyrolysis reactor, PID controller, electrically heated furnace, glass condenser and measuring cylinder. The temperature of the furnace was maintained by highly sensitive PID controller.

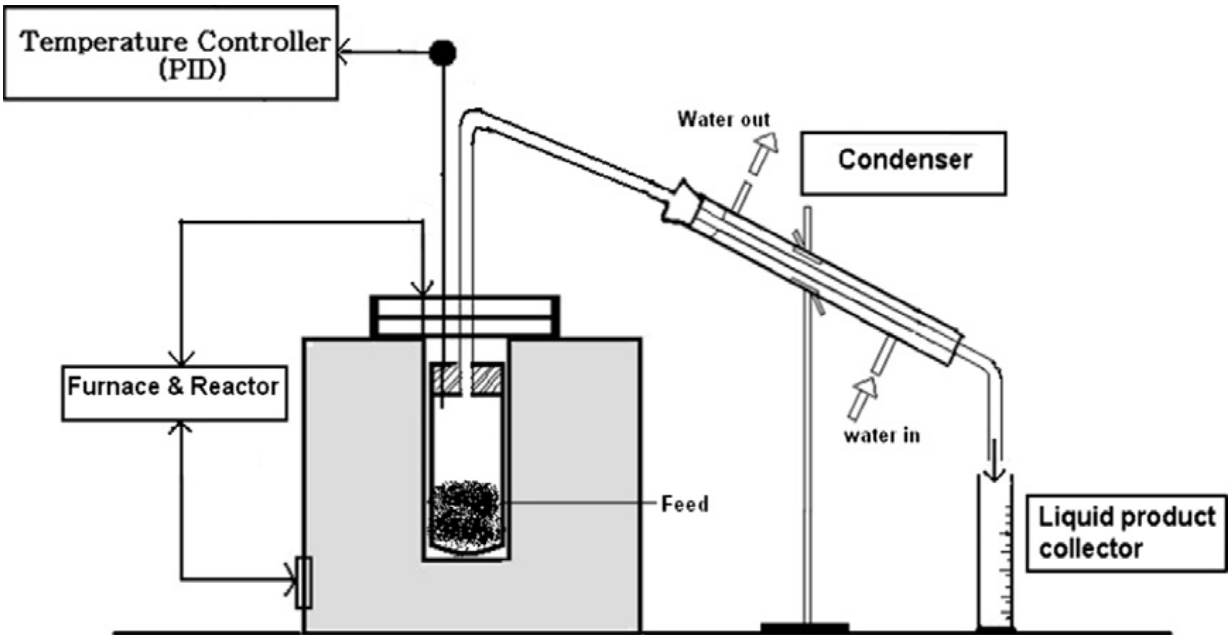


Fig.3.4:- the schematic diagram of the pyrolysis experimental set-up.

3.5 REACTOR SPECIFICATION

The reactor (Fig. 3.6) is cylindrical shaped vessel made up of stainless steel having capacity of ½ liter. The pyrolysis experiments were performed in an apparatus designed with a batch reactor of height 16.5cm, 4.7 cm ID and OD 5.0 cm. in diameter. The reactor was externally heated by an electric furnace in which the temperature is measured by a thermocouple a Cr-Al:K type thermocouple fixed inside the reactor. The temperature of the furnace is maintained by a highly sensitive PID controller.

Fig. 3.5 Reactor

3.6 PYROLYSIS PROCEDURE:

Pyrolysis experiment was carried out for Jatropha seed at different temperatures starting from 300℃ to 700℃ at 50℃ intervals. The experiment was allowed to continue for at least 20 min after the oil production ceased. The rate of heating was kept at 20℃/min. For each sample run amount of liquid produced and char remained in the reactor were noted. The temperature at which the amount of bio fuel production became maximum is the optimum temperature. Two additional runs were carried out at Temperatures equal to optimum temperature$\pm 25^{o}$C

The liquid products were condensed by using water bath. The temperature is measured by Fig.1 shows the schematic diagram of the pyrolysis experimental set-up. The connecting pipe between the reactor and the trapping system was heated to 400°C to avoid condensation of tar vapor. Water is circulated as cooling medium in the condenser through a pump. The condensed vapors are collected in a container as the liquid product whereas there is some amount of non-condensable gases which are simply left out. The liquid product collected in the measuring cylinder contains bio oil and oily water. This Oily water is basically water with some dissolved nitrogen and oxygen containing hydrocarbons. Bio oil and Oily water are further separated in a gravity separator as they form two separate layers of liquid because of difference in density.

Fig.3.6.1:- Bio oil in measuring cylinder

Fig.3.6.2 Gravity separator

3.7:- CHARACTERIZATION OF BIO DIESEL OBTAINED

The physical properties such as pour point, viscosity, density, flash point, calorific value, fire point, color of all pyrolytic oil were determined and mentioned in the result and discussion part.

3.7.1:- DETERMINATION OF FUNCTIONAL GROUP OF PYROLYTIC OIL

Fourier Transform Infrared spectroscopy (FTIR) of pyrolytic oil obtained at temperature of 500^{o}C was analyzed using a Perkin-Elmer infrared spectrometer and in the range of 400-4000cm^{-1} with a resolution of 4cm^{-1} to know the presence various functional groups. Various groups are listed in the discussion part.

3.7.2:- GC-MS ANALYSIS OF PYROLYTIC OIL

GC-MS was carried out to find out the chemical compounds present in the pyrolytic oil using GC-MS-OP 2010[SHIMADZU] analyzer.

3.7.3:- CHARACTERIZATION OF PYROLYTIC CHAR

SEM analysis of the pyrolytic char was done to find out their average pore diameter.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF RAW MATERIALS

Proximate and ultimate analyses were used to characterize the raw material. This determines the Ash, Moisture, fixed carbon, volatile matter contents in the fuel. It is a quick and practical way of grading fuels based on quality and type. The moisture content of biomass has a remarkable effect on the conversion efficiency and heating value. Higher moisture of biomass has an increasing tendency to decompose resulting in energy loss during storage. Volatile matter evolves in the form of light hydrocarbon, tars and gas. Volatile matter of the biomass is higher than the coal (around 75%). It has higher volatile matter which makes it more readily devolatilized than solid fuel. So, Liberation of less fixed carbon makes them more useful for pyrolysis and gasification. The moisture content and ash content affect the heating value significantly by reducing calorific value. The ash content in the bio mass is an integral part of plant structure which consists of a wide range of mineral matter such as salt of Ca, K, Si and Mg. Ash content mainly depends upon the plant and soil condition in which the plant grows. This shows that the raw material contains higher percentage of volatile matter and less amount of moisture and ash content and higher weight percentage of oxygen followed by carbon and hydrogen with a fewer amount of sulphur. Proximate analysis is given in table 4.1.

Table.4.1.1:- Proximate analysis of Jatropha seed

Composition\raw material	Jatropha seed
% volatile matter	82.03
%moisture	5.9
% ash content	7.9
% fixed carbon	4.16

Table.4.1.2:-Ultimate analysis of Jatropha seed

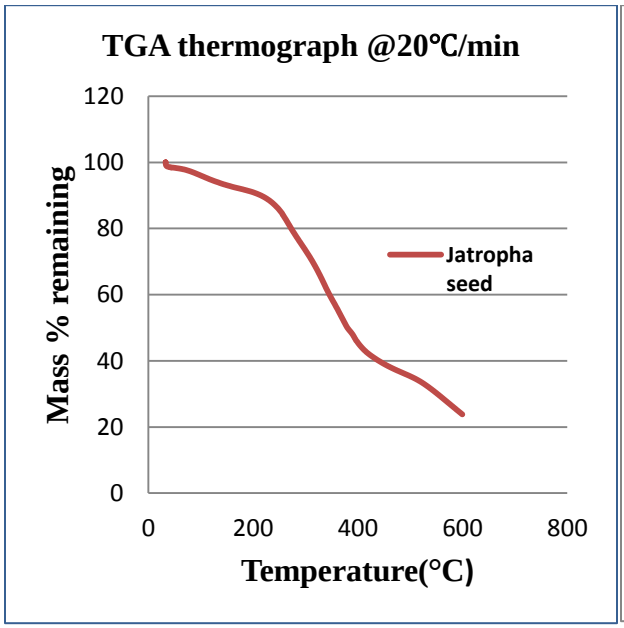
material\composition	Carbon %	Hydrogen %	Nitrogen %	Sulphur %	C/H ratio	C/N ratio
Jatropha seed	56.55	4.23	4.68	1.08	12.33	12.08

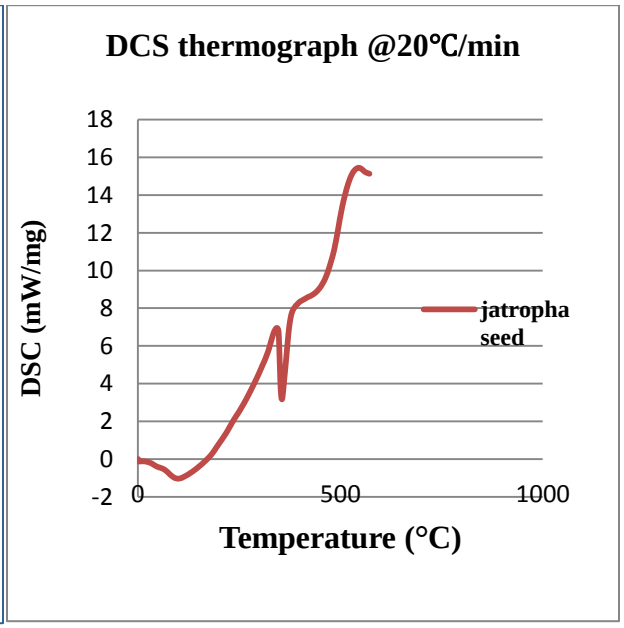
4.2:-THERMO GRAVIMETRIC ANALYSIS OF RAW MATERIALS (TGA)

Thermo gravimetric analysis (TGA) is used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. Most experiments with TGA provide a thermograph that has three main different phases: drying, devolatilization in inert atmosphere and combustion in oxygen [35].The TGA thermograph of jatropha seed at a heating rate of 20^{o}C/min under air atmosphere is shown in Fig. 4.2 whereas DCS thermograph is shown in Fig. 4.2. The characteristic parameters of devolatilization are presented in this section. It is observed that weight loss occured in three stages. The initial decomposition or 1st. decomposition occurred between 35 to 200^{o}C for both feeds. That represents up to 5-10 % weight loss at the heating rate of 20^{o}C/ min. The rapid decomposition, the 2nd decomposition of the sample occurred between 200 to 500^{o}C representing an 70% weight loss. The 1st. stage decomposition represents the evaporation of moisture contents, 2nd. Decomposition indicates the formation of volatiles mainly. In the 3rd stage, the pyrolysis residue slowly decomposes, with the weight loss velocity becoming smaller and smaller and the residue ratio tends to become constant at the end the hydrocarbon decomposition. Due to high decomposition rate, the rapid decomposition zone or 2nd stage of decomposition is treated as active pyrolytic zone. During 2nd stage, the intermolecular associations and weaker chemical bonds are broken. The side aliphatic chains are broken and some small gaseous molecules are produced because of the lower temperature. During the 3rd stage chemical bonds are broken at higher temperature and the parent molecular skeletons are destroyed. As a result, the larger molecule degrades in to smaller molecules in the form of gaseous phase. Finally char remains. [1-5].

It is observed from the DCS thermograph that during 1st stage of decomposition, it lies in 3rd quadrant which proves that moisture is removed during this stage. Then as the heating proceeds, during pyrolytic zone evolution of heat (exothermic cracking reactions) leads the curve to the 1st quadrant.

Fig. 4.2.1:- TGA thermograph of Jatropha seed Fig.4.2.2:- DCS thermograph of Jatropha seed





4.3:- INFLUENCE OF TEMPERATURE ON PRODUCT YIELD

Fig. 4.3.1 shows the product yielded at a heating rate of 20℃/ min for pyrolysis of Jatropha seed. It is observed that the yield of liquid product increases with increase in temperature but up to a certain temperature (500℃ for Jatropha seed). Then it decreases with increase in temperature due to the formation of more amounts of non condensable gases/volatiles. As the temperature increases the char yield gets decreased because of the secondary reaction taking place at the third stage of pyrolysis, which means the char materials decomposes at higher temperature. [6-17]

In case of Jatropha seed pyrolysis, the liquid yield increased from 26.34 to 67% by weight as the temperature raised from 300-500^{o}C and then started to decrease. After temperature 500^{o}C, when pyrolysis temperature increased to 550^{o}C the density of oil increased means the weight of oil was more with the same volume oil. It may be due to the formation of denser products at high temperature and lower residence time of feed materials in the reactor. So, 500^{o}C is the appropriate temperature for pyrolysis of Jatropha seed to get maximum yield of oil. Two additional runs were carried out at 475^{o}C and 525^{o}C to check the optimality. It is seen that it follows the same trend i.e. increases to become maximum at 500^{o}C and then decrease because of over cracking.

Table.4.3.1:- Influence of temperature on pyrolysis of Jatropha seed

Temperature(°C)	% of liquid product	% of char	% of gaseous product
350	26.34	48.32	25.34
400	29.13	47.63	23.34
450	50.06	29	20.94
475	51.9	28.56	19.6
500	67	28.76	4.5
525	52.7	26	21.3
550	50.96	27.4	21.64

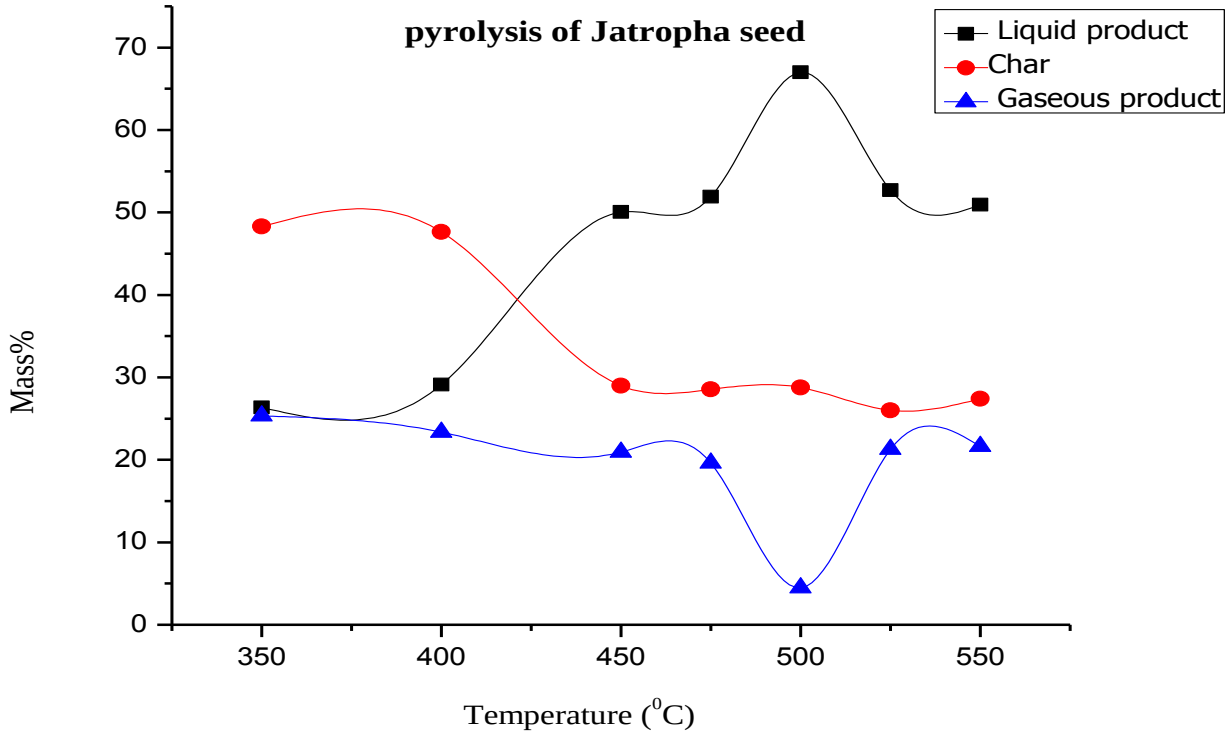


Fig. 4.3.1:-Effect of temperature on pyrolysis Jatropha seed

4.4:- FRACTIONATION OF PYROLYTIC OIL

The oil obtained from pyrolysis is separated into two fractions based on their density difference in a gravity separator as shown in Fig. 3.6.2. The upper dense layer is fuel layer and bottom heavy layer is the aqueous layer. The upper part can be used as alternative to fuel and the bottom layer is a mixture of water and some fractions of organic liquids mostly carbohydrate derived compounds. The fuel properties of the top layer are given in Table. The aqueous extract of bio oil includes both low molecular weight aldehydes that are effective meat browning agent (especially glycol aldehyde) as well as phenolic compounds that provide a smoky flavors. A potential application of the water soluble fraction of bio oil is the production of salt of calcium carboxylic acid that can be used as ecofriendly road deicers. The water insoluble fraction that usually constitutes 25- 30% of the whole bio-oil is often called pyrolytic lignin because it is essentially composed of oligomeric fragments originating from degradation of native lignin. [18] So the pyrolytic oil obtained from pyrolysis of jatropha seed is valuable from fuel and chemical point of view. (Table 4.3, 4.6, 4.7)

4.5:-CHARACTERIZATION OF BIOFUEL

4.5.1:- CHNS ANALYSIS OF JATROPHA SEED PYROLYTIC OIL:

Ultimate analysis of Jatropha seed pyrolytic oil was done to find the elemental composition of bio-oil and to determine its empherical formula and are compared with diesel in Table.12.

Table.4.5.1:- Ultimate analysis of Jatropha seed pyrolytic oil

Element	Jatropha seed oil	Diesel
C	62.38	85.72
H	5.27	13.2
N	5.24	0.18
S	1.85	0.3
O	25.26	0.6
H/C molar ratio	8.4	1.85
Empherical formula	$CH_{1.013}N_{1.008}S_{0.3558}O_{4.8592}$	$CH_{1.847}N_{0.0017}S_{0.0013}O_{0.00524}$
Calorific value (MJ/Kg)	13.55	43.8

The CHNO analysis of the pyrolytic oil shows that it contains maximum amount of C, H and O. Higher the C/H ratio shows the oil having good calorific value, can be observed from the Tables 4.5.1.

4.5.2:- FTIR (FOURIER TRANSFORM INFRARED SPECTROSCOPY)

This is an important analysis technique which detects presence and various characteristic of functional groups present in the bio oil. This technique is used to obtain an infrared spectrum of absorption, emission, photoconductivity of a solid, liquid or gas. The term FTIR originates from the fact that a Fourier transformation is required to convert the raw data into the actual spectrum. This measures how well a sample absorbs light at each wavelength. The most convenient way to do this is allowing a monochromatic light beam to fall on a sample and then measuring how much energy is absorbed into it. On interaction of an infrared light with oil, chemical bond will contract, stretch and absorb infrared radiation in a specific wave length range regardless molecular structure based on this principle functional group present in the pyrolytic oil is identified. The FTIR spectra were collected in the range of 400-4000 cm^{-1} region the resolution being $8cm^{-1}$. The FTIR imaging is done using Perkin Elmer RX.

Table.4.5.2:- Functional groups present in Jatropha seed pyrolytic oil

Wave number(cm -1)	Type of vibration	Nature of functional group
409.10	C-H Bending	Alkenes
1424.59	C-H Bending/ scissoring	Alkanes
1643.96	C= C Stretching	Alkenes
2108.03	C=O Stretching	Aldehydes/Ketones
2348.23	O-H Stretching	Carboxylic acids and derivatives
3413.19	N-H Weak	Amines

C-H bending/stretching vibrations at 409.10 cm^{-1} detect the presence of alkenes. C-H stretching at 1424.59 cm^{-1} shows presence of alkanes. C=C stretching vibrations at 1643.96 cm^{-1} shows the presence of alkenes. The N-H weak vibrations at 3413.44 cm^{-1} indicates the presence

of amines. O-H stretching at 2348.23 cm^{-1} shows the presence of carboxylic acids and derivatives. The results were found consistent with the literature and when compared with GC-MS.

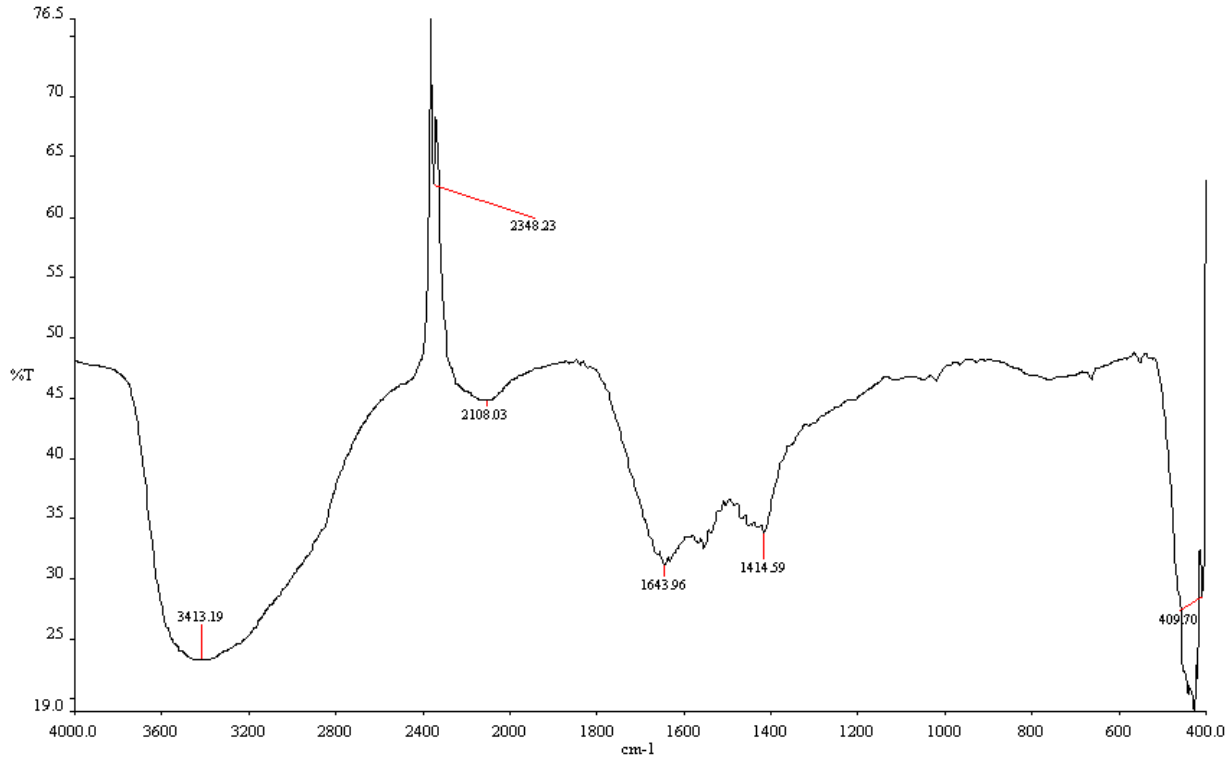


Fig.4.5.1:- FTIR spectrum of Jatropha seed bio-oil.

4.5.3:-GC-MS (GAS CHROMATOGRAPHY MASS SPECTROMETRY)

GC-MS is used both for the qualitative and quantitative analysis bio fuel. This measures the amount of volatile and semi volatile organic compounds in complex mixtures. The pyrolytic oil obtained was characterized by using GC/MS- QP 2010 SHIMADZU and with flame ionization and mass spectrometry detection. A capillary tube (L=30m and D=0.25mm) coated with a 0.25 um film of DB-5 with was used. Helium gas (99.99% purity) was used as carrier gas at flow rate of 1.50 ml/min. The oven initial temperature was set to 70^0C for 2 min and then increased to 300^0C at a rate of 10^0C/min and maintained for 7-8 min. All the compounds were identified by means of the NIST 11.l library. The major compound of Jatropha seed pyrolytic oil was characterized by GC-MS at a pyrolytic temperature of 400^0C and 550^0C is given in Table.4.5.3. Different types of compounds such as normal alkanes, alkenes, saturated fatty acids and their derivatives such as esters, amides and nitriles were identified. All the compounds were

classified with increase in retention time. Figure 4.5.3 shows the GC-MS images of Jatropha seed pyrolytic oil.

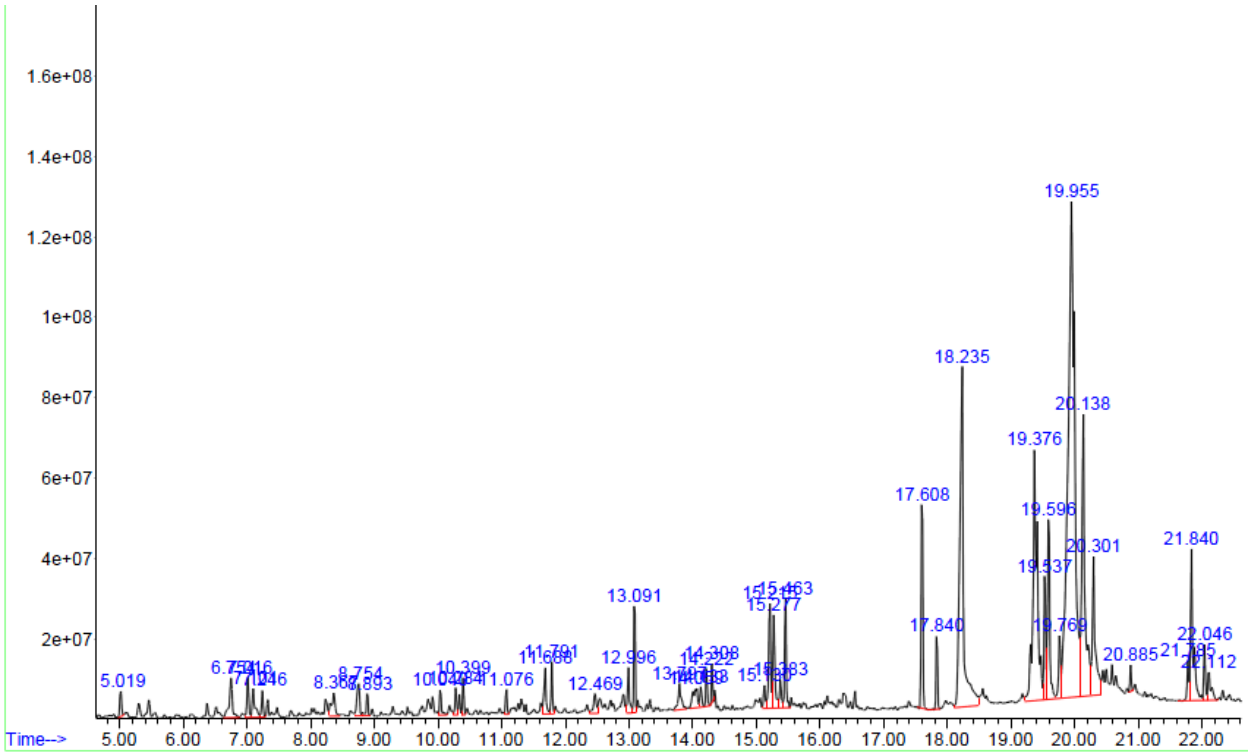


Fig.4.5.3 Spectrum of GC of Jatropha seed pyrolytic oil

The major compounds present in the oil as obtained from the graph are at area% of 29.49, 11.52, 9.64, 8.10 and the compounds were identified as Oleic acid, n-Hexadecanoic acid, Oleanitrile, Octadecanoic acid. So these compounds can be separated and some value added substances can be made which can be marketed. Oleic acid is an emulsifying agent and used in manufacture of soap. It is also used as moisturizer, excipient in pharmaceuticals and solubilizing agent in aerosol products. Phenol m-pentadecyl is used as a raw material for surfactants, antioxidants, lubricant additives, co-solvent for insecticides, germicides and coupling agents. n-Hexadecanoic acid is one of the most common saturated fatty acid used as enzyme inhibitor. Enzyme inhibitors are agents that combine with an enzyme in such a manner as to prevent the normal substrate-enzyme combination and the catalytic reaction by blocking the active site. It can be observed that the bio-oil contains 22 compounds in the range of C6 – C20 which is present in most of the fuels.

Table.4.5.3:- GC-Mass composition of the major compounds in bio-oils Jatropha seed.

R. Time	Area %	Name of compound	Molecular formula
5.018	0.43	phenol	C_6H_6O
6.747	1.14	p-Cresol	C_7H_8O
7.023	0.65	2-methoxy Phenol	$C_7H_8O_2$
7.095	0.70	1-Undecene	$C_{11}H_{22}$
7.240	0.38	Undecane	$C_{11}H_{24}$
8.373	0.80	1-methyl-4-butyl Benzene	$C_{11}H_{16}$
8.751	0.81	1-Dodecene	$C_{12}H_{24}$
8.896	0.40	Dodecane	$C_{12}H_{26}$
10.043	0.44	4-ethyl-2-methoxy-Phenol	$C_9H_{12}O_2$
10.290	0.39	1-Tridecene	$C_{14}H_{28}$
10.406	0.45	Tridecane	$C_{13}H_{28}$
11.074	0.36	2,6-dimethoxy- Phenol	$C_8H_{10}O_3$
11.684	0.89	2-Tetradecene	$C_{14}H_{28}$
11.786	0.64	Tetradecane	$C_{14}H_{30}$
12.469	0.50	Cyclotetradecane	$C_{14}H_{28}$
12.991	0.79	1-Pentadecene	$C_{15}H_{30}$
13.093	1.65	Pentadecane	$C_{15}H_{30}$
13.790	0.71	n-Nonylcyclohexane	$C_{15}H_{30}$
14.066	0.81	7-Hexadecene,	$C_{16}C_{32}$
14.139	0.37	3-Hexadecene	$C_{16}C_{32}$

14.226	0.50	Z-8-Hexadecene	$C_{16}H_{32}$
14.313	0.40	Hexadecane	$C_{16}H_{34}$
15.126	0.36	8-Dodecen-1-ol	$C_{12}H_{24}O$
15.214	1.92	8-Heptadecene	$C_{17}H_{34}$
15.388	0.48	E-14-Hexadecenal	$C1_6H_{30}O$
15.460	1.67	Heptadecane	$C_{17}H_{36}$
17.610	3.25	Pentadecanenitrile	$C_{15}H_{29}N$
17.842	1.04	Hexadecanoic acid	$C_{17}H_{32}O_2$
18.234	11.52	n-Hexadecanoic acid	$C1_7H_{32}O_2$
19.382	9.64	Oleanitrile	$C_{18}H_{33}N$
19.541	1.92	9-Octadecenoic acid	$C_{18}H_{36}O_2$
19.599	3.82	Octadecanenitrile	$C_{18}H_{35}N$
19.774	1.20	Methyl stearate	$C_{19}H_{38}O$
19.948	29.49	Oleic Acid	$C_{18}H_{34}O_2$
20.137	8.10	Octadecanoic acid	$C_{18}H_{36}O_2$
20.297	3.62	Hexadecanamide	$C_{16}H_{33}NO$
20.892	0.30	9-Octadecenoic acid	$C_{18}H_{36}O_2$
21.778	0.55	9,12-Octadecadienoic acid	$C_{18}H_{34}O_2$
21.836	3.53	9-Octadecenamide	$C_{18}H_{35}NO$
22.039	0.80	Octadecanamide	$C_{18}H_{35}NO$
22.112	0.81	N,N-dibutyl-3-cyclope Propanamide	$C_{29}H_{39}N_3O$

4.5.4:- PHYSICAL PROPERTIES

Characterization of pyrolytic oil obtained by the pyrolysis of jatropha seed is done according to their physical/fuel properties as described in the experimental section. The physical properties of fuel layer are given here. Table 4.5 shows the optimum temperatures of pyrolysis to get maximum volumetric yield and the comparison between cotton seed cake and jatropha seed pyrolytic oil with diesel. The colour and odour of all pyrolytic oil was dark reddish brown and a distinctive smoky smell. Pyrolytic oil was separated into two layers light fuel layer and heavy aqueous layer. All physical properties like flash point, fire point, density, viscosity and calorific value are comparable with diesel. These bio oils are soluble with petroleum products like petrol, diesel, toluene and methanol; also the calorific values are very near to diesel. So the pyrolytic oil is comparable with diesel and can be used with addition to diesel in transportation processes.

Physical properties of Jatropha seed pyrolytic oil (JSPO) were found out by standard test methods and are compared commercial diesel (CD) is given in Table.4.5.4. Kinematic viscosity of JCPO is much greater than CD and this is due to the presence of glycerides or polymers that are found in cooking oil.

Table 4.5.4:-Comparison of physical properties of Jatropha seed bio-diesel and commercial diesel.

Characteristic	Jatropha seed pyrolytic oil(JSPO)	Commercial Diesel(CD)
Appearance	Dark brown oil	Yellowish
Specific gravity(15C/15 C)	0.91	0.84
Kinematic viscosity@ 40 ^{0}C in cst	49.72	2.7
Flash point (^{0}C)	56	60
Fire point (^{0}C)	80	65
Cloud point (^{0}C)	22	-40
Pour point (^{0}C)	18	-16
Gross calorific value(MJ/Kg)	13.55	42.5
Conradson carbon residue	14.35%	<0.15%

Sulfur content	--	1.2
Acidity as mg of KOH/g	85.34	0.20

Table 4.5.5:- Calorific value comparison of jatropha seed and jatropha oil

Material	Calorific value(cal/gm)
Jatropha seed	3226.19
Jatropha oil	7329

4.5.6:- SEM ANALYSIS

SEM-EDX is a high magnification imaging technique for making a quantitative chemical analysis of unknown materials. The SEM can perform analysis of particles of size of up to 2 μm with the advantage of chemical characterization using EDX (find out elemental composition of materials.)

Scanning electron microscopy images were taken by using JEOL (JSM-6480 LV) microscope having an acceleration voltage of 15 kV, equipped with a 6587 EDX scanning spectrometry detector. SEM analysis was done to find the surface morphology of char and are shown in Fig.4.5.6.1-Fig.4.5.6.4 are of Jatropha seed char taken at 500X magnification. These images showed heterogeneous distribution of pores and rough texture. The average pore sizes present on the char surface of the char was found to be 15 μm. This shows that these chars can be good surfactants being highly porous.

Fig.4.5.6.1:- SEM of Jatropha pyrolytic char

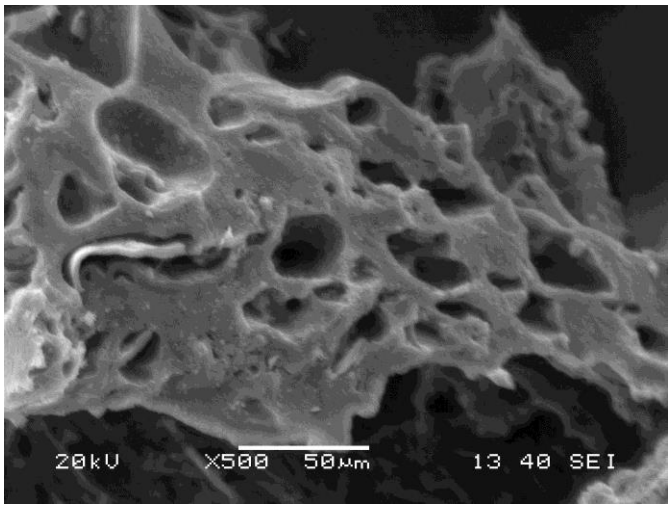
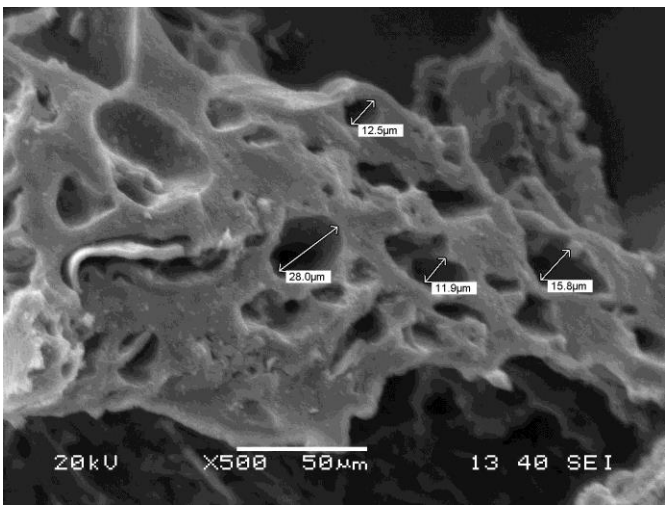


Fig.4.5.6.2:-SEM of Jatropha pyrolytic char



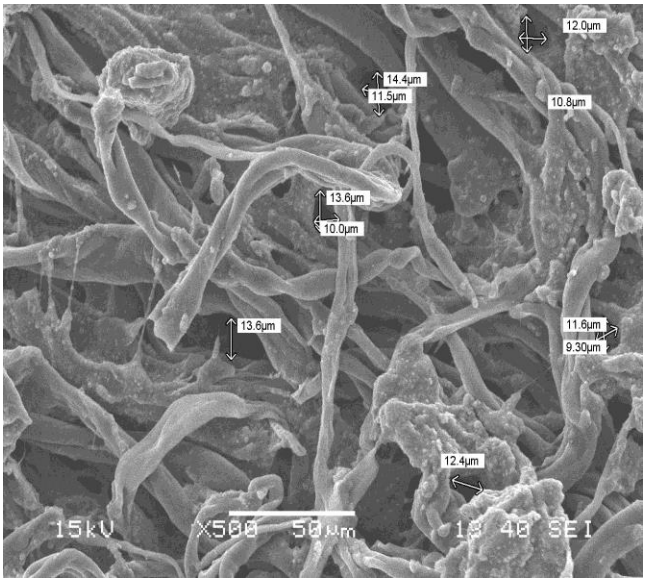


Fig.4.5.6.3:-SEM of Jatropha pyrolytic char

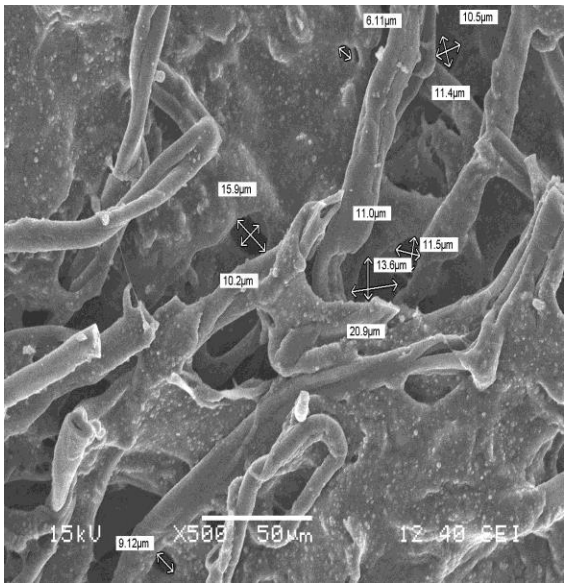


Fig.4.5.6.4:-SEM of Jatropha pyrolytic char

CHAPTER 5

CONCLUSION

In this study, Jatropha seed was taken as a biomass sample and pyrolysis experiments was done in a semi batch reactor under different temperatures of 350-600^{0}C to obtain maximum yield of bio-oil. Since our aim was to maximize the oil content we have to operate the pyrolysis reaction at the optimum pyrolysis temperature of 500℃. It was essential to study the characteristics of the bio oil produced. Various physical properties like flash point, viscosity, density, pour point, presence of various functional groups were found out and compared to that of petrol and diesel. The oil produced in this biomass pyrolysis can be upgraded to improve its octane number and then can be supplied as replacement of the fossil fuels.

The following conclusions can be drawn from this work:

• The maximum bio-oil yield was 50% at an optimum temperature of 500^{0}C for Jatropha seed. It is very significant from the above fig.4.2.1 that as the pyrolysis temperature increased, the amount of liquid product also increased up to a certain value and then it decreased because of formation of excessive gaseous product.

• Char yield decreased with increase in temperature, the gaseous yield decreased initially, became optimum at the point where the liquid is maximized and then increased because of excessive cracking. This shows that temperature has significant effect on pyrolysis yields and conversion efficiencies.

• FTIR analysis showed that the bio-oils contain large amount of oxygen and nitrogen bearing groups (carboxylic and amines) apart from the presence of straight chain alkanes and alkenes. Presence of Oxygen in fuel is not desirable, so they are to be removed to obtain good efficient fuels.

• GC-MS analysis showed the presence of about 40 chemical compounds in the bio –oil of different carbon molecules. Separation and analysis of these materials may lead to major industrial applications as various value added products can be obtained and marketed.

• Presence of pores shown by SEM analysis gives the scope of using this char as an adsorbent after enhancing surface characteristics by chemically treatment.

Chemical characterization of the bio-oil showed that, it can be effective synthetic fuels and source of chemical feedstock.

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